

An ecological risk assessment of heavy metal pollution of the agricultural ecosystem near a lead-acid battery factory

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ABSTRACT

Lead-acid battery factories can lead to heavy metal pollution of nearby agricultural ecosystems. To assess the ecological risk and to understand the transport processes of heavy metals in an agricultural ecosystem, the concentrations of heavy metals in agricultural soils (As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn) and in wheat plants at different stages of growth (Cd, Pb, and Zn) were investigated near the Fengfan lead-acid battery factory in Baoding, China. Certain indices, including the contamination factor (C_f), pollution load index (PLI), hazard quotient (HQ) and hazard index (HI), were used to assess the ecological risk of the agricultural soil and human health risk. The results show that the mean concentrations of the heavy metals studied in the surface soils were all lower than the guideline values of China. However, the C_f values of Pb ranged from 2.8 to 5.3, indicating that the most examined soils were strongly impacted by Pb. The PLI range was 0.6–4.2, indicating moderate contamination levels for those most examined soil samples. The As, Cr, Cu, Mn and Ni in the studied area were geogenic elements and Cd, Pb and Zn were mainly derived from the lead-acid battery factory based on the results of a principal component analysis (PCA) and heavy metal spatial distribution. The elements Cd, Pb and Zn entered the soil through atmospheric deposition and accumulated mainly as a bioavailable fraction at the surface. With respect to wheat berries, only the mean Pb content exceeds the tolerance for Pb at 0.84 mg/kg, indicating a potential risk. In relation to health risk, the HQs of individual heavy metals for different exposure populations were all lower than 1, showing a much lower potential health risk. Nevertheless, the potential health risk due to the cumulative risk of all heavy metals through the consumption of wheat berries exceeded unity for rural populations.

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1. Introduction

Heavy metals are easily discharged into an agricultural ecosystem due to common human activities, and this results in an adverse impact on the ecosystem. An agricultural ecosystem has a close relationship with human health, thus, heavy metal pollution of agricultural ecosystem has been of concern throughout the world (Bermudez et al., 2011, 2012; Pandey and Pandey, 2008). Heavy metals, as traditional pollutants, are highly toxic, non-degradable and bioaccumulative. Although some heavy metals such as Zn and Cu are essential elements for plants and humans as catalytic com-

ponents of proteins and enzymes, the great majority of them do not have any beneficial physiological function, and their excess accumulation in the human body can lead to many diseases (Godt et al., 2006). For example, accumulation of Cd in the human body can lead to kidney, bone and pulmonary damage (Godt et al., 2006); Pb can damage the central nervous system, kidneys and blood system (Tong et al., 2000), etc. The diet is a main route of exposure to heavy metals for most people except for occupational exposures at related industries (Sharma et al., 2008). There are many famous cases of heavy metals poisoning through the food chain such as “Itai-Itai” disease in Japan in the 1930s and “minamata disease” in Japan in the 1950s. It has been well known that agricultural soils contaminated by heavy metals and atmospheric metal deposition can result in high levels of heavy metals in crops (Bermudez et al., 2012; Harrison and Chirgawi, 1989; Pandey and Pandey, 2008; Sharma et al., 2008). Accordingly, the ecological

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assessment for heavy metal pollution of agricultural ecosystems is important.

The heavy metal pollution of an agricultural ecosystem is often caused by waste water irrigation, solid waste disposal, vehicular exhaust, fertilisation, industrial activities, etc. (Cheng, 2003; Khan et al., 2008; Liu et al., 2011, 2012). Among these pollution sources, industrial activities are the dominant sources of heavy metals near factories. Kabala and Singh (2001) reported that, in the vicinity of a copper smelter in Poland, the concentrations of Cu, Pb and Zn in the surface soils were significantly higher than their concentrations in the subsurface soils. It was reported that industrial waste can lead to heavy metal pollution of the surrounding soils (Gowd et al., 2010). In China, with the rapid industrial development of recent decades, the heavy metal pollution of soil has become more and more severe. Production of lead-acid batteries is one of the main sources of heavy metals. In China, production of lead-acid battery output is very high, which was 90.77 million kilovolt-ampere-hour (kVAh) accounting for about one-third of the total world output in 2008 (Chen et al., 2012). The Fengfan lead-acid battery factory is famous in China. It was founded more than a decade ago in Baoding City. The long-term production of lead-acid batteries may cause heavy metal pollution of the agricultural ecosystem near the factory.

Wheat is one of the main crops grown for human consumption in the north of China, which provides some carbohydrates, proteins and certain inorganic micronutrients for the human body. Therefore, high concentrations of heavy metals in the wheat berry may lead to severe potential risk for human health. To guarantee food safety, the Food and Agriculture Organization (FAO), World Health Organization (WHO), the Health Ministry of China and other organisations strictly regulate the allowable concentrations or maximum permitted concentrations of toxic heavy metals in food-stuffs (MHPRC, 1992, 2005; Codex Alimentarius Commission, 1995). The hazard quotient (HQ) and hazard index (HI) have also been proposed by the United States Environmental Protection Agency (USEPA) to assess the potential human health risk induced by heavy metals (USEPA, 1989). This method compares the estimated dose of a contaminant with the reference dose and has been widely used to assess potential human health risk (Bermudez et al., 2011; Huang et al., 2008).

In this paper, the objectives were (i) to obtain As, Cd, Cr, Cu, Mn, Ni, Pb and Zn distributions, bioavailability and mobility in agricultural soils near a lead-acid battery factory; (ii) to investigate Cd, Pb and Zn concentrations in wheat and the heavy metal relationship between the soil and plants; and (iii) to assess the ecological risk to the agricultural ecosystem and the human health risk induced by Cd, Pb and Zn.

2. Materials and methods

2.1. Studied area and sampling

Baoding city, located in the North China plain, has a temperate monsoon climate with an average annual temperature and rainfall of 12 °C and 550 mm, respectively. Agricultural soil samples were collected near Fengfan's non-ferrous metal branch (the lead-acid battery factory) in Baoding city, which was founded in 1995. This general manufacturing plant mainly produces lead alloys, lead-acid batteries and accessories. The annual production capacity of this battery factory has reached 3.5 million KVAh.

The soil samples were collected from the farmland situated to the east of the factory, because it was surrounded by residential areas and roads to the west, north and south. To the north of the study area, there is a pit, into which some household garbage and agricultural waste are deposited. The specific locations of the sampling sites were shown in Fig. 1. A total of 34 surface

soil samples, including one background soil sample and 33 soil samples for analysis to the east of the lead-acid battery factory, were collected from the topsoil (0–10 cm) at each sampling site. The location of the background soil site is to the east of the factory approximately 500 meters (N 38°47'32.10", E 115°30'8.18"). Soil core samples of 50 cm length were collected at sites S4, S5, S6, S11, S12 and S13 using a soil column sampler (Beijing New Landmark Soil Equipment Co. Ltd.) and sliced into specimens with a height of 5 cm. All soil samples were air-dried, grounded into a fine power and sieved through a 0.149 mm polyethylene sieve for further analysis. Wheat samples were also collected at the same sites as the soil samples. In all, 33 wheat plants at the tillering stage, 22 wheat plants at the jointing stage and 22 wheat berry samples were collected. The wheat samples were first washed with tap water to eliminate ash on the leaves and soil on the roots, and then washed with distilled water. The wheat plants were divided into above-ground parts, below-ground parts and grains, and then dried at 60 °C in an oven to constant weight. The dried wheat samples were ground into a powder for analysis.

2.2. Chemical analysis

The main physicochemical properties of the surface soil samples were characterised by the following methods: soil pH was measured using a pH meter (Mettler Toledo FE20, Switzerland) (soil:water = 1:2.5); organic matter (OM) was measured by the K₂Cr₂O₇ oxidation method (Nanjing Institute of Soil Science, 1978); cation exchange capacity (CEC) was investigated by the BaCl₂ compulsive exchange method (Gillman and Sumpter, 1986) and particle-size distribution was obtained using a laser particle size analyser (Microtrac S3500, America). The soil samples were digested with HNO₃–HClO₄–HF (3:1:1, v/v), and the concentrations of heavy metals were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES) (Jarrell-ASH ICAP-9000, USA). The wheat samples were digested with H₂O₂–HNO₃ (1:1, v/v) and the contents of Cd, Pb and Zn were determined similarly with ICP-AES. The analytical quality control was based on the geochemical standard soil (GSS-1 and GSS-2), the certificate of the certified reference material “bush twigs and leaves” (GSV-1) and wheat flour (GBW08503b) provided by the National Standard detection Research Center of China. In the process of soil and plant sample digestion, each batch of samples included some standards and one blank in order to assure the quality. The analytical results and the certified values of the standards shown in Supplementary materials (Suppl. Table 1) did not differ significantly, which suggested that the data obtained is credible.

The Cd, Pb and Zn speciation of the six soil cores was determined by following the modified Community Bureau of Reference (BCR) sequential extraction procedure. The modified BCR method can be briefly described as follows: For the exchangeable and carbonates fraction (F1): 20 mL of 0.11 mol/L acetic acid solution was added to 0.5 g soil samples and shaken for 16 h at 22 ± 5 °C. The extract was separated from the solid residue by centrifugation at 5000 × g for 20 min. For the reducible fraction (F2): 20 mL of 0.1 mol/L hydroxylamine hydrochloride solution adjusted to pH 2.0 with HNO₃ was added to the residue from step 1 in the centrifuge tube, and the mixture was shaken at 22 ± 5 °C for 16 h. The extract was separated as in step 1. For the oxidisable fraction (F3): 5 mL of 8.8 mol/L H₂O₂ was added to the residue from the second step and digested for 1 h at 22 ± 5 °C and for 1 h at 85 ± 5 °C until the volume was reduced to approximately 1.5 mL. Another 5 mL of H₂O₂ was added, and digested for 1 h at 85 ± 5 °C until the volume was reduced to 1 mL. The residue was extracted with 25 mL 1 mol/L ammonium acetate solution adjusted to pH 2.0, and shaken for 16 h at 22 ± 5 °C. The extract was separated as described above. The full details of the procedure have been previously reported (Rauret

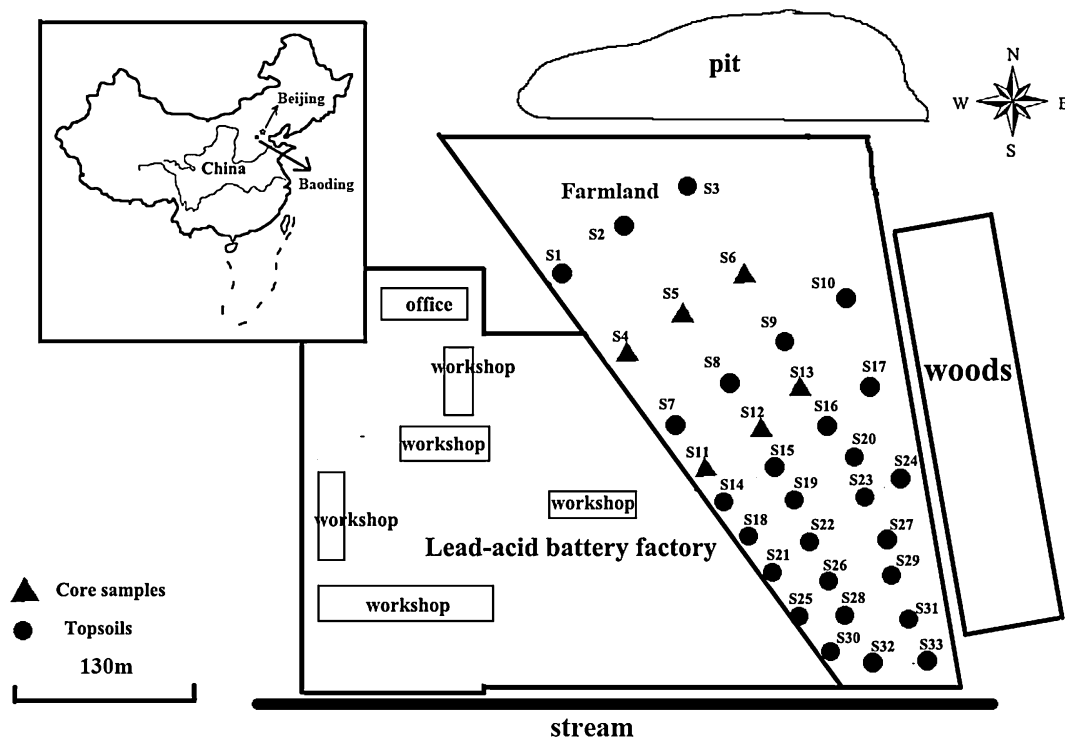


Fig. 1. Locations of the study area and sampling sites.

et al., 1999; Sahuquillo et al., 1999). The difference between the total concentration and the sum of the F1, F2 and F3 fractions was taken as the residual fraction (F4). Sediment reference material BCR-701 was extracted using the modified BCR method to assess the quality of the data. The analytical results and the certified values presented in Supplementary materials (Suppl. Table 2) did not differ significantly.

2.3. Statistical analysis and spatial distribution maps

Principal component analysis (PCA) and linear regression analysis were carried out with the statistical software package SPSS version 20.0 for Windows. In the PCA, a VARIMAX normalised rotation with Kaiser Normalisation was applied based on the correlation matrix. Statistical significance was defined at the 95% level in the linear regression analysis. In addition, contour maps of heavy metals and contamination levels were made using the power interpolation technique in SURFER v.10.0 (Golden Software Inc., CO, USA).

2.4. Assessment of soil pollution

The contamination factor (C_f) is defined as the ratio of heavy metal concentration in the soil to the background value:

$$C_f = \frac{C_{\text{heavy metals}}}{C_{\text{background}}} \quad (1)$$

The contamination levels were classified by their intensities, ranging from 1 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderate to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong) (Muller, 1969). To examine the overall level of soil pollution across the sampling sites, the pollution load index (PLI) had been determined as (Bhuiyan et al., 2010):

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} \times \dots \times C_{fn})^{1/n} \quad (2)$$

where n is the number of samples.

The PLI is a simple and useful means for assessing the level of heavy metal pollution. Four pollution levels were defined: no

pollution ($PLI < 1$), moderate pollution ($1 < PLI < 2$), heavy pollution ($2 < PLI < 3$), and extremely heavy pollution ($3 < PLI$).

2.5. Bioconcentration factor (BCF)

The BCF of metals in the soil to the aerial part of the plants or grain was defined as the ratio of the heavy metal concentration in the plants to that in the soil:

$$BCF = \frac{C_{\text{wheat}}}{C_{\text{soil}}} \quad (3)$$

2.6. HQ and HI

The HQ was used to express the potential non-cancer risk for individual heavy metals (USEPA, 1989).

$$HQ = \frac{CDI}{RfDo} \quad (4)$$

$$CDI = \frac{CF \times IR \times EF \times ED}{BW \times AT} \quad (5)$$

where the chronic daily intake (CDI) is the exposure expressed as the mass of a substance contacted per unit body weight per unit time, averaged over a long period of time; RfDo represents safe levels of exposure by oral intake for a lifetime; CF is the median concentration of heavy metals in wheat berries (mg/kg). IR is the ingestion rate of wheat berries (kg/(person day)). In this study, IRs obtained from a daily study of Hebei province of China (Zhang et al., 2011), are 140.1 g/(person day) and 256.2 g/(person day) for urban and rural adults, respectively. The daily intake of wheat for children was assumed to be 1/3 of that for adults, so IR for urban and rural children were 46.7 g/(person day) and 85.4 g/(person day), respectively. The EF is the exposure frequency (365 days/year). ED is the exposure duration (assumed as 70 years for adults and 6 years for children), equivalent to the average lifetime (Huang et al., 2008). The BW is the average body weight (61.6 and 18.6 kg for adults and children, respectively (Zhu et al., 2011). The AT is the average exposure time for non-carcinogenic effects ($ED \times 365$ days/year). If the

HQ is less than 1, then there are no obvious non-cancer effects. If HQ is equal to or higher than 1, there may be potential non-cancer effects.

The RfDo value represents safe levels of exposure by oral intake for a life time. The RfDo of Cd and Zn were established by USEPA (2000). The values of RfDo are 0.001 mg/kg/day and 0.3 mg/kg/day for Cd and Zn, respectively. The RfDo for Pb has not yet been established (USEPA, 2004). In this paper, 0.004 mg/kg/day was used by reference from the study of Huang et al. (2008) who calculated the RfDo of Pb based on the recommendation of an intake limit by FAO/WHO (FAO/WHO, 1984).

To assess the overall potential health risk imposed by more than one heavy metal, USEPA has proposed an HI based on USEPA's

guidelines for health risk assessment of chemical mixtures (USEPA, 1986). This HI is given as:

$$HI = \sum HQ = \frac{CDI_1}{RfDo_1} + \frac{CDI_2}{RfDo_2} + \dots + \frac{CDI_i}{RfDo_i} \quad (6)$$

3. Results and discussion

3.1. Distribution and source of heavy metals in the surface soils

3.1.1. Properties and heavy metal distribution of the surface soils

The physicochemical properties of the soil were not significantly different among the studied surface soil samples. With the

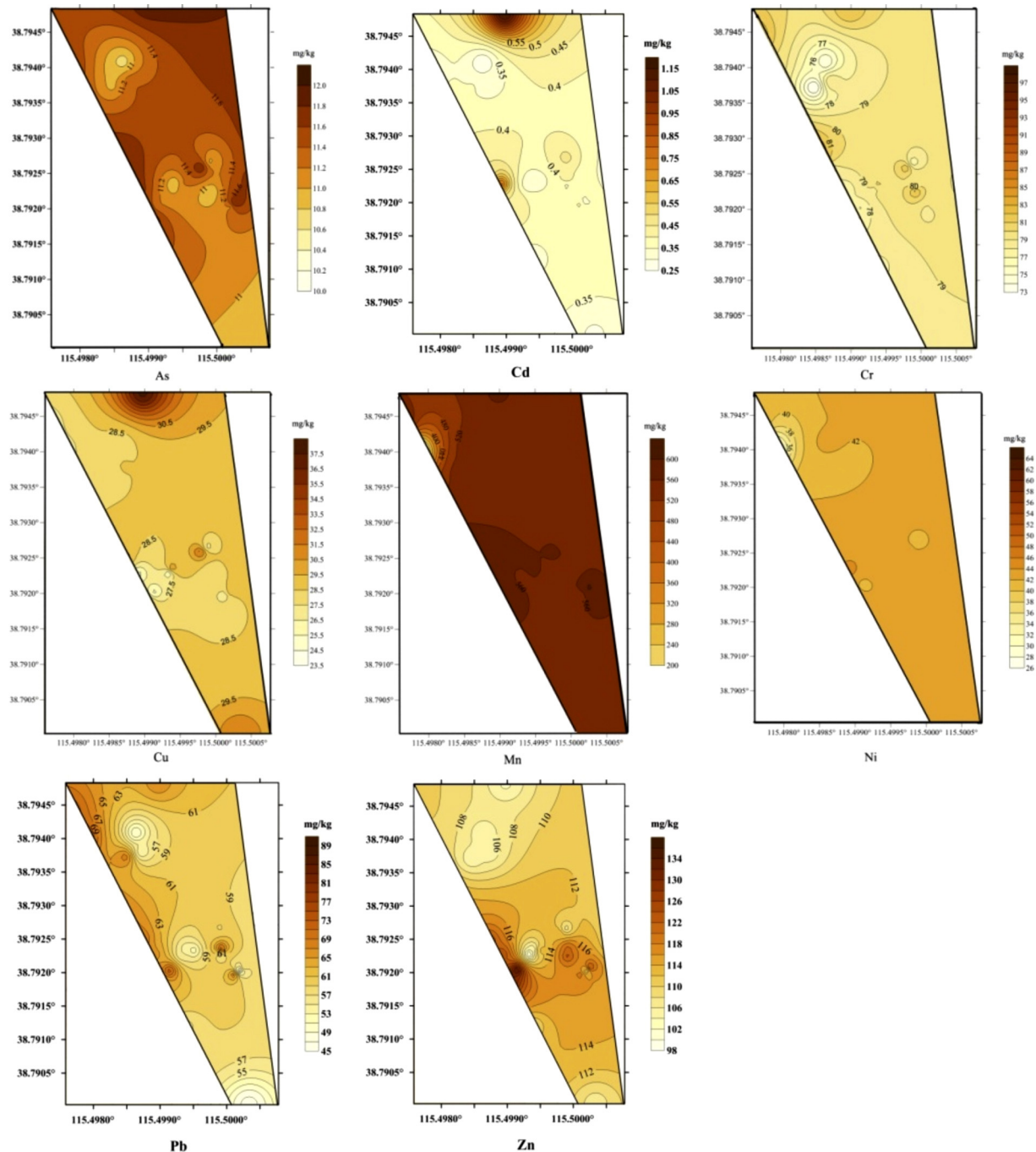


Fig. 2. Heavy metal distribution of the surface soils at the studied area.

exception of the background soil, the mean values were 8.06 ± 0.08 for pH, 23.09 ± 3.06 g/kg for OM, 17.18 ± 0.96 cmol_c/kg for CEC, $3.92 \pm 0.96\%$ for clay, $32.44 \pm 2.19\%$ for silt and $63.64 \pm 2.51\%$ for sand, respectively.

The heavy metal concentrations of the surface and background soils were shown in Table 1. The mean concentrations of heavy metals were all lower than the guideline values of China (MEPC, 1995) with 11.3 ± 0.4 mg/kg for As, 0.39 ± 0.17 mg/kg for Cd, 79.5 ± 4.4 mg/kg for Cr, 28.6 ± 2.7 mg/kg for Cu, 561.5 ± 23.4 mg/kg for Mn, 42.3 ± 3.7 mg/kg for Ni, 61.2 ± 9.7 mg/kg for Pb, and 113.4 ± 8.8 mg/kg for Zn, respectively. The results indicated that the pollution level of the studied heavy metals in the study area was not very serious. The contents of As, Cr, Mn and Ni in the surface soils were comparable to the background values, while the contents of other heavy metals were higher than the background values. Further, the Cd content of the soil at site S7 was 0.77 mg/kg, which is higher than the guideline value of China. It is noted that the concentrations of Cd and Pb in soil samples were 2.6 and 3.7 times higher than their background soil concentrations, respectively. This suggests that Cd and Pb have accumulated in surface soil.

Based on the contour maps of As, Cr, Cu, Mn and Ni (Fig. 2), the concentrations of these elements were generally invariant in the studied area, indicating less impact by human activities. However, contour maps of Cd, Pb and Zn showed that concentrations of these elements in the surface soils near the lead-acid battery factory, were high, and decreased gradually with the distance from the factory (Fig. 2). It indicates that the lead-acid battery factory is the dominant source of Cd, Pb and Zn. The main process in the factory is to grind lead block for the production of lead-acid batteries. Air pollution control equipment has been used during lead-acid battery production, however, the incomplete removal of dust results in dust emission. In previous studies, atmospheric metal deposition has been found to have a positive correlation with the heavy metal concentrations of surface soil (Onianwa and Fakayode, 2000; Sharma et al., 2008). Dusts containing heavy metals from the lead-acid battery factory are gradually deposited on the surface soils under the effects of wind and gravity. In the Baoding district, while the predominant wind direction varies with season, winds in the northeast-southwest direction are the dominant. Atmospheric metal deposition in this wind direction may be the reason of the unique distribution patterns of Cd, Pb and Zn in the studied area. Similar results had also been reported previously (Chen et al., 2012; Hernandez et al., 2003; Rodríguez et al., 2009). In addition, there was a hotspot of Cd and Cu in the northern part of the studied farmland. To the north of the study area, there is a pit, in which some household garbage and agricultural waste are deposited. Household garbage always contains some electronic waste and metal material because garbage segregation is not common in the country of China. Electronic waste contains many toxic heavy metals such as Cd and Cu (Guo et al., 2010). This may be responsible for the high concentration of Cd and Cu in the northern part of the study area.

3.1.2. Source analysis of heavy metals in the surface soils

To further identify the source of heavy metals in the agricultural soil, a PCA analysis was performed, which has been considered to be an effective tool for source identification of heavy metals (Anju and Banerjee, 2012; Bai et al., 2010). Three principal components were obtained (Table 2 and Fig. 3), and those accounted for 77.947% of all the total variation. The elements As, Cr, Cu and Ni were included in the first principal component (PC1) explaining the greatest variance (34.229%); the second principal component (PC2) was composed of Cd, Pb and Zn explaining 27.838% of the variance. The third principal component (PC3) only included Mn, explaining 15.879% of the total variance.

The geogenic elements were considered to be As, Cr and Ni in the surface soils in many previous studies (Hanesch et al., 2001;

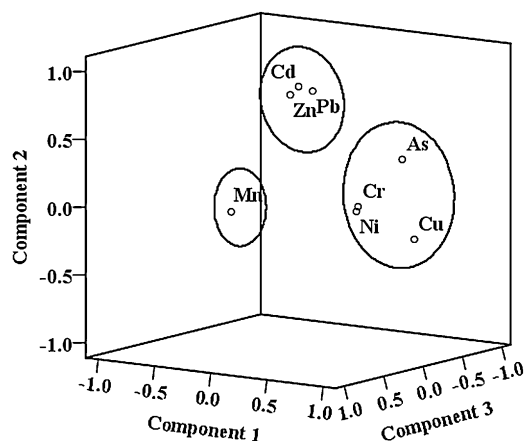


Fig. 3. PCA of heavy metals for the studied soils.

Liu et al., 2011). Moreover, their distribution patterns were generally invariant in the studied area. Although Mn was individually included in the PC3, the distribution of Mn in the studied soils confirmed that it derived from the parent materials of the soil. Cu was also included in PC1 because the concentration of Cu was generally invariant in the surface soil and similar with As, Cr, Mn and Ni as discussed above. Based on the distribution pattern of Cd, Pb and Zn in the surface soil, PC2 including Cd, Pb and Zn were mainly impacted by dust deposition from the lead-acid battery factory. The results of the PCA were consistent with heavy metal distribution in the studied soil and this further confirmed the source of heavy metals in the studied area.

3.2. Distribution of heavy metals in the soil cores

Because As, Cr, Cu, Mn and Ni in the surface soils were geogenic elements as discussed above, only Cd, Pb and Zn in the soil cores were subjected to speciation research. The vertical distribution of their speciation in soil cores was shown in Fig. 4. The mean concentrations of heavy metal speciation of the six soil cores were used because a significant difference between the six soil cores was not found. For the total concentrations of heavy metals, the striking pattern was that the concentrations of Cd, Pb and Zn in the soil profiles decreased gradually with depth in the surface soil (0–20 cm) while becoming constant in the subsurface soil (20–50 cm). The results of the Cd and Pb distribution in the soil profiles suggest that the concentrations of Cd and Pb in the agricultural soils have been significantly impacted by lead-acid battery production. Although the Cd, Pb and Zn concentrations had the similar vertical distribution patterns, only the total concentration of Zn in the subsurface soils was significantly lower than that in the background surface soil. The subsurface soils were less likely to be polluted, so the background surface soil was also slightly polluted by Zn. Cultivation activities, such as fertilisation, might cause an accumulation of Zn in the background surface soil (Liu et al., 2011). Nevertheless, the Zn concentration in the studied surface soils was slightly higher than its background value, indicating that lead-acid battery production also contributed to the Zn accumulation in the surface soils. The pattern of vertical distribution of heavy metals simultaneously indicated that heavy metals that have accumulated in the surface soils transport slowly to the subsurface soils under the present conditions such as rain, irrigation and other cultivation activities. Some previous research has shown that heavy metals can be transported by water which can result in adverse effects on groundwater (Basta and McGowan, 2004; Li and Shuman, 1996). However, the results showed no significant transportation of heavy metals from surface to subsurface soils in the studied area, and the groundwater

Table 1
Concentrations of heavy metals in the surface agricultural soils (mg/kg).

	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Min.	10.1	0.25	72.9	23.9	520.0	40.0	46.0	99.4
Max.	12.0	1.15	99.2	37.8	616.1	62.7	89.0	134.2
Mean	11.3	0.39	79.5	28.6	561.5	43.2	61.2	113.4
S.D.	0.4	0.17	4.4	2.7	23.4	3.7	9.7	8.8
Guideline values of China ^a	25	0.6	250	100	–	60	350	300
Background values	9.6	0.15	71.4	18.5	591.0	38.5	16.7	104.0

^a The value of guideline values of China (pH > 7.5, dry land soil).

Table 2
Total variance explained and rotated component matrix for heavy metals in the surface soils.

Component	Initial eigenvalues			Rotation sums of squared loadings			Elements	Component		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %		1	2	3
1	3.017	37.707	37.707	2.738	34.229	34.229	As	0.800	0.359	−0.177
2	2.052	25.653	63.361	2.227	27.838	62.067	Cd	0.069	0.862	0.093
3	1.167	14.586	77.947	1.270	15.879	77.947	Cr	0.835	0.103	0.433
4	0.610	7.630	85.577				Cu	0.858	−0.234	−0.248
5	0.533	6.665	92.242				Mn	0.039	0.052	0.906
6	0.368	4.605	96.848				Ni	0.798	0.059	0.400
7	0.161	2.012	98.859				Pb	0.134	0.823	0.008
8	0.091	1.141	100.000				Zn	−0.056	0.778	0.020

Extraction method: principal component analysis; rotation method: Varimax with Kaiser Normalisation. Rotation converged in six iterations.

quality was unlikely to be influenced. This is not surprising because the study area is located in an arid and semi-arid region with not much rainfall, and the irrigation water, mainly consisting of rain and groundwater, often evaporates before it permeates into very deeply.

The bioavailability and mobility of heavy metals in the soil have a significant relationship to their speciation in the soil. The F1 fraction is known as the most bioavailable fraction, but the F4 fraction is held within their crystal structure, which is unlikely to be released (Nemati et al., 2011; Rodríguez et al., 2009). As shown in Fig. 4, in the surface soil (0–10 cm), the contents of the F1 fraction were 0.09, 1.81 and 9.10 mg/kg for Cd, Pb and Zn, respectively. The content of the F1 fraction was higher in the surface soil than in the subsurface soil. A high content of bioavailable heavy metal in the surface soil can produce a heavy metal pollution risk for groundwater and food (Basta and McGowen, 2004; Kabala and Singh, 2001; Li and Shuman, 1996). For the different heavy metals studied, the proportion order of the F1 fraction was Cd (28.4%) > Zn (9.9%) > Pb (3.1%) in the surface soil (0–10 cm). It has been reported that the bioavailability proportion of Cd in soils and sediments is relatively high (Delgado et al., 2011; Pueyo et al., 2008). Previous studies have also shown that the mobility of Zn in soils is higher than that of Pb

(Rodríguez et al., 2009; Wilson and Pyatt, 2007). In addition, a significant proportion of Pb was found in the F2 fraction, which was consistent with previous studies (Liu et al., 2013; Rodríguez et al., 2009). The hydrous oxides of Fe and Mn have a particularly high affinity for Pb and play an important role in controlling their mobility in the environment (Ma and Uren, 1998; Rodríguez et al., 2009; Wang et al., 2013). In the soil cores, the F4 fraction was dominant in the subsurface. It is worth noting that the content of the F4 fraction was not significantly different between surface and subsurface soil, while the content of the F1 and F2 fractions were decreased with depth. The results indicated that once an external source of heavy metals has gotten into the soil, more heavy metals exist as bioavailable fraction, and the transformation rate of heavy metals from the bioavailable to the residual fraction is very slow.

3.3. Heavy metals in the wheat

The concentrations of Cd, Pb and Zn in wheat berries and wheat plants of two different growth stages were presented in Table 3. For the wheat of the tillering stage, the concentrations of Cd, Pb and Zn were 0.40 ± 0.18 , 17.63 ± 8.86 and 84.32 ± 26.50 mg/kg in the aerial part and 0.33 ± 0.15 , 5.43 ± 5.03 and 132.39 ± 26.33 mg/kg in

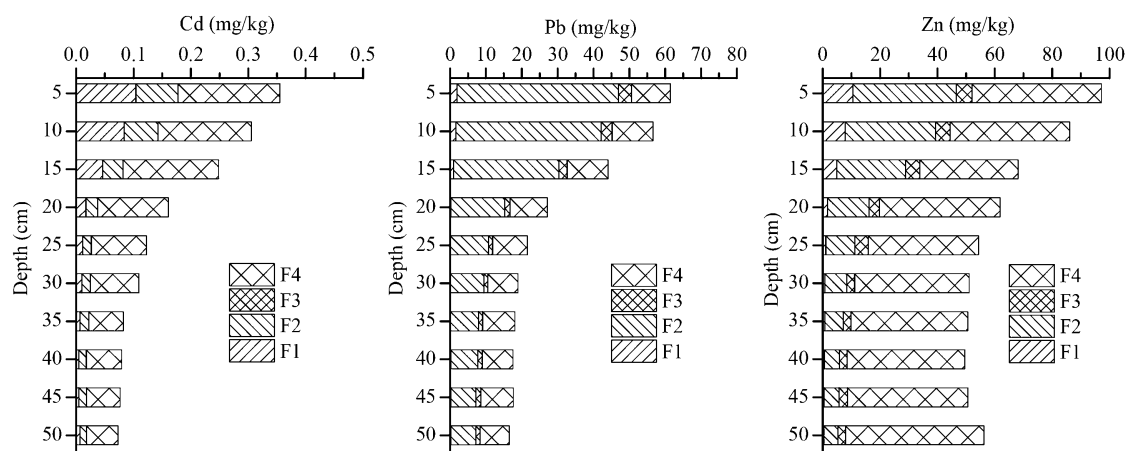


Fig. 4. Vertical distribution of heavy metal speciation in the soil cores.

Table 3
Concentrations and transfer factors of heavy metals in wheat.

		Cd (mg/kg)	BCF	Pb (mg/kg)	BCF	Zn (mg/kg)	BCF
Tillering stage	Aerial part	0.40 ± 0.18	1.09 ± 0.43	17.63 ± 8.86	0.29 ± 0.13	84.32 ± 26.50	0.74 ± 0.20
	Underground part	0.33 ± 0.15		5.43 ± 5.03		132.39 ± 26.33	
Jointing stage	Aerial part	0.18 ± 0.09	0.52 ± 0.26	13.56 ± 6.91	0.22 ± 0.10	46.92 ± 9.27	0.42 ± 0.08
	Underground part	0.39 ± 0.14		26.89 ± 9.52		109.47 ± 29.06	
Maturity stage	Grains	0.06 ± 0.02	0.17 ± 0.06	0.84 ± 0.47	0.01 ± 0.01	41.30 ± 5.16	0.37 ± 0.05
	Tolerance limits	0.1 ^{a,b}		0.2 ^{a,b}		50 ^b	

^a FAO/WHO.
^b Ministry of health of PRC (China).

the underground part, respectively. These results indicated that, during wheat tillering, Cd and Pb accumulated more in the aerial part than the underground part. However, wheat in the jointing stages accumulated more heavy metals in the underground part than the aerial part. For wheat berries, the mean concentrations of Cd and Zn (0.06 and 41.3 mg/kg, respectively) were all lower than

the tolerance limits, while the mean content of Pb (0.84 mg/kg) in the wheat berries far exceeded the tolerance limit, indicating a potential risk to human health.

The BCF values for heavy metals were calculated based on the ratio of metal concentrations in plants (aerial part or grains) to soil. As shown in Table 3, the orders of BCF, in all growth stages,

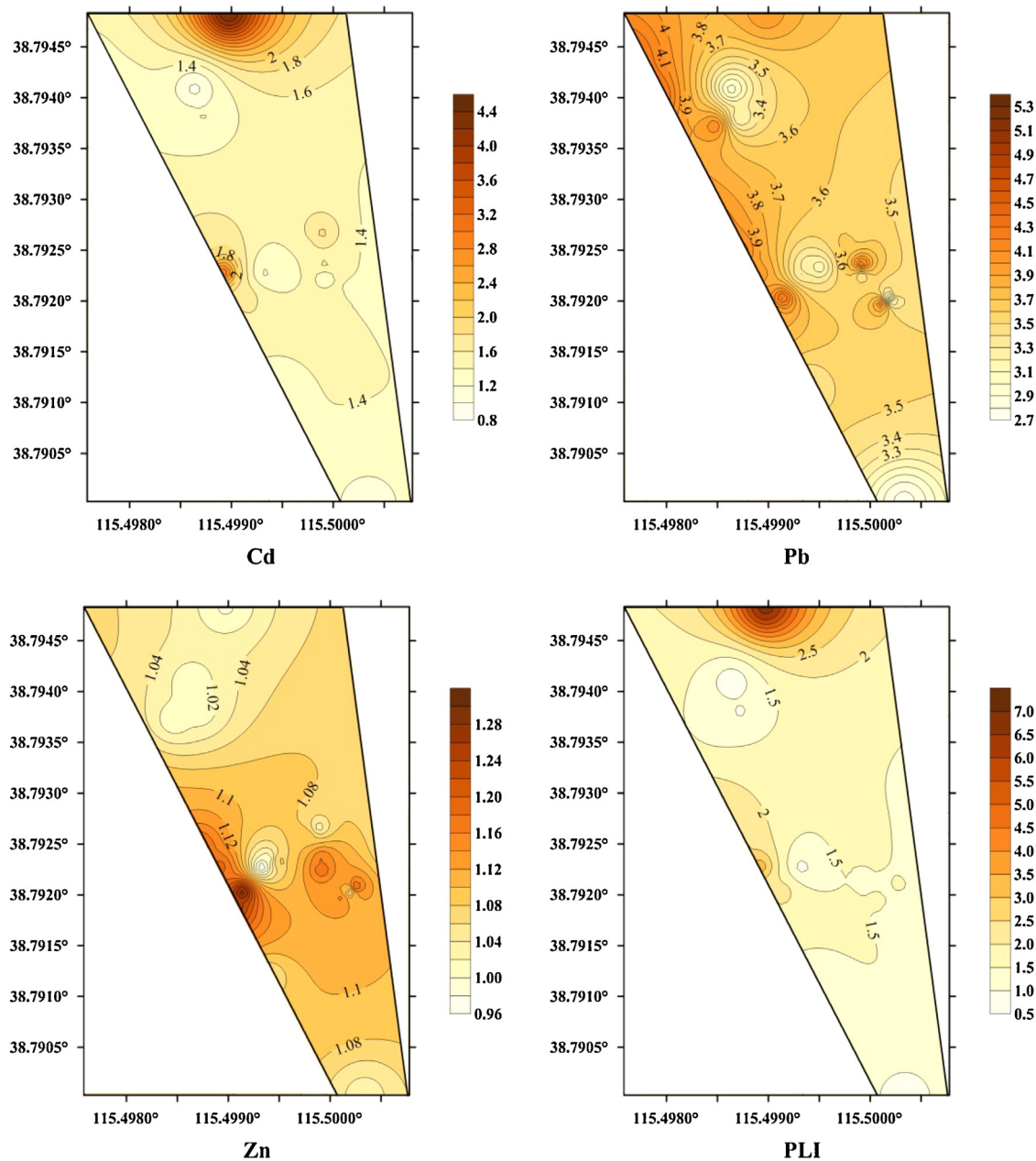


Fig. 5. Distribution of C_f and PLI at the studied area.

is the same with $Cd > Zn > Pb$. It is worth noting that the orders of BCF are consistent with the percentage of the heavy metal F1 fraction in the surface soil. The F1 fraction as the most bioavailable fraction includes the exchangeable and carbonates fraction, which weakly adsorb on the soil surface and precipitate or co-precipitate as carbonates (Filgueiras et al., 2004; Rodríguez et al., 2009). The order of BCF suggested that the bioavailability of heavy metals was one of the important factors impacting on the BCF of plants. The BCF of wheat berries was lower than the other two growth stages with 0.17, 0.01 and 0.37 for Cd, Pb and Zn, respectively. This result suggested a lesser impact of heavy metals on wheat berries.

It is well known that high contents of heavy metals in soils can significantly contribute to their contents in crops, resulting in adverse effect on human health. Accordingly, the relationship between total heavy metal concentrations in the soil and in the wheat grain was examined using linear regression analysis. Although none of the correlations between heavy metal concentrations in the soils and in the wheat berries were statistically significant ($p > 0.05$), the concentrations of Cd and Pb in the wheat berries had a positive correlation with those in the soils (Suppl. Fig. 1). The correlation between Zn concentrations in the soils and in the wheat berries was very low. Atmospheric metal deposition is one of the important factors resulting in the accumulation of heavy metals in plants (Bermudez et al., 2012; Berthelsen et al., 1995; Pandey and Pandey, 2008; Sharma et al., 2008). Bi et al. (2009) found that foliar uptake of atmospheric Pb was the dominant path way for Pb to enter the leaf and grain tissues of maize grown around a zinc smelter based on Pb isotope analysis. Further, the speciation of heavy metals in the soil and soil properties also impact this relationship (Nannoni et al., 2011). These may explain why we found no statistically significant correlations between the total concentrations of Cd, Pb and Zn in the soils and in the wheat berries.

3.4. Ecological risk assessment for heavy metal pollution of surface soils

In view of the pollution by heavy metals including only Cd, Pb and Zn, the ecological risk assessment of them for agricultural soils were carried out by C_f and PLI. The contour maps of C_f and PLI were shown in Fig. 5. The mean values of C_f were 1.4, 3.7 and 1.1 for Cd, Pb and Zn, respectively. In most soil samples, the C_f of Cd ranged from 1 to 2, and contamination levels were none to medium. The C_f of Pb ranged from 2.8 to 5.3 indicating that most examined soils were strongly polluted by Pb. The Zn contamination level of the surface soil was not serious with the C_f values ranging from 1.0 to 1.3. The C_f of the studied heavy metals had the highest values in the agricultural soils near the factory and gradually decreased with the distance from the factory.

The range of PLI was 0.6–4.2, and the contamination levels of most examined soils were moderate ($1 < PLI < 2$). The soils near the factory were heavy ($2 < PLI < 3$) or extremely heavy ($3 < PLI$) polluted. In contrast, the contamination levels of soils, in the western part of the study area, were moderate. This suggests that the lead-acid battery factory had caused some extent risk of the studied area.

3.5. Health risk of consuming wheat berries

The heavy metal contamination of wheat and the potential health risk, induced by lead-acid battery factory, were carried out by HQs and HIs (Table 4). For different heavy metals, the order of HQs was $Pb > Zn > Cd$. For different exposure populations, the HQs of individual heavy metals were all lower than 1. This indicated that the daily intake of individual metals through the consumption of wheat berries was unlikely to cause an adverse health risk. For the different groups of people, the HQs of adults were higher

Table 4

HQs and HIs of individual heavy metals for different exposure populations.

	Urban adults	Urban children	Rural adults	Rural children
Cd	0.12	0.13	0.22	0.25
Pb	0.37	0.41	0.68	0.75
Zn	0.31	0.34	0.56	0.62
HI	0.80	0.88	1.46	1.62

than that of children, and the HQs of urban people were lower than that of rural people. The order of heavy metal HQs was rural children $>$ rural adults $>$ urban children $>$ urban adults. These results were in agreement with previous studies (Huang et al., 2008; Zhu et al., 2011).

The HIs of the heavy metals were 0.80, 0.88, 1.46 and 1.62 for urban adults, urban children, rural adults and rural children, respectively. Although no single metal HQs exceeded the unity, the cumulative risk of all heavy metals through the consumption of wheat berries exceeded unity for the group of rural people. It indicated that there may be a potential health risk for rural people. Moreover, the HIs of urban people were below 1, suggesting that urban inhabitants are unlikely to be affected by heavy metals through consuming wheat berries from the studied area.

4. Conclusions

The heavy metal transport and ecological risk assessment of an agricultural ecosystem were studied near a lead-acid battery factory. The mean concentrations of the studied heavy metals in surface soils were all lower than the guideline values of China, but the concentrations of Cd, Cu, Pb and Zn were higher than the background values. The results of PCA and heavy metal distribution indicated that As, Cr, Cu, Mn and Ni in the soils mainly originated from the parent material of the soil, and Cd, Pb and Zn concentrations were obviously impacted by lead-acid battery factory. The external Cd, Pb and Zn accumulated mainly in the surface soil, and exist as a bioavailable fraction (F1 and F2) in the surface soil suggesting some extent potential risk. With respect to the wheat berries, only the mean content of Pb in wheat berries exceeded the tolerance limit, indicating a potential health risk. The order of BCF, the same for all growth stages of wheat, was $Cd > Zn > Pb$. It was also the same with the proportion of the bioavailable fraction of heavy metals in the surface soil. Nevertheless, no significant correlation of heavy metals was found between soil and grains, which suggested leaf uptake of heavy metals through atmospheric metal deposition was one of the important ways of entering plant. The results of an ecological risk assessment showed that, compared with the background soil, heavy metal contamination levels of most surface soils were moderate, and the Pb contamination in the study area was most severe. Regarding health risk, the HQs of the individual heavy metals were all lower than 1, indicating low potential health risk. The order of the heavy metal HQs was rural children $>$ rural adults $>$ urban children $>$ urban adults. Nevertheless, the potential risk due to a cumulative risk of Cd, Pb and Zn through consumption of wheat berries exceeded unity for groups of rural people.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ecolind.2014.04.040>.

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